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Ganzeveld, K.J.; Capel, J.E.; Wal, D.J. van der; Janssen, L.P.B.M.

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THE MODELLING OF COUNTER-ROTATING TWIN SCREW EXTRUDERS AS REACTORS FOR SINGLE-COMPONENT REACTIONS

K. J. GANZVELD, J. E. CAPEL, D. J. VAN DER WAL and L. P. B. M. JANSSEN[†]

Department of Chemical Engineering, Groningen University, Groningen, The Netherlands

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Abstract—Numerical models are useful to study the behaviour of the extruder as a polymerization reactor. With a correct numerical model a theoretical analysis of the influence of several reaction and extruder parameters can be made, the limitations of the use of the extruder reactor can be determined and the effects of scale-up can be studied. The numerical model developed for a single-component reaction in a twin screw extruder shows good agreement with experimental data for the polymerization of *n*-butylmethacrylate during the reactive extrusion process. At low rotation rates a disagreement may occur between experiments and predicted data. However, the program is very useful for industrial scale processes where extruders operate in the area of high rotational speeds.

INTRODUCTION

Models for reactive extrusion are important to study the effect of operating conditions and geometric parameters on the progress of the reaction. With accurate numerical models, predictions can be made about the extruder behaviour, scale-up effects of the process can be studied in detail and expensive experiments can, to some extent, be omitted. Numerical modelling therefore plays an important role in the study of the extruder as a reactor (Stuber and Tirrel, 1985; Speur *et al.*, 1987 and Speur, 1988). Both authors, mentioned above, tried to model the extruder reactor leading to two similar models, based on the ideal mixed reactor approximation. Major imperfections of these models are the use of kinetic and extruder constants in the model which were determined by trial and error, or by using data and relations not applicable to the reaction studied. Therefore, the model results have no physical basis and cannot predict the ongoing process in the extruder.

In this paper an extended and improved numerical model of the extruder reactor for a one-component reaction is presented and discussed, using parameter values which have, as far as possible, a physical meaning. The obtained model is validated by comparing model results with experimentally obtained data for the polymerization of *n*-butylmethacrylate.

THE WORKING MECHANISM OF A COUNTER-ROTATING TWIN SCREW EXTRUDER

A counter-rotating twin screw extruder, as used in this work, is closely intermeshing and consists of series of C-shaped chambers in which material is

transported towards the die. Interaction between the chambers occurs through the leakage gaps (Fig. 1). The leakage gaps are divided into four groups (Janssen, 1978):

- the flight gap (Q_f). This is a clearance between the barrel and the flight of the screws.
- the tetrahedron gap (Q_t). Between the flight walls a gap exists having approximately the shape of a tetrahedron. This gap connects the consecutive chambers on the opposite screws.
- the calender gap (Q_c). This gap is formed by the clearance between the flight of one screw and the bottom of the channel of the other screw and resembles a calender.
- the side gap (Q_s). This is a gap between the flanks of the flights of the two screws.

Often, a monomer or pre-polymer is fed in liquid form to the extruder reactor. Due to this liquid feed two zones can be distinguished:

- A partially filled zone where the chambers are still not completely filled with material.
- The pump zone, completely filled with material where pressure is built up and where the material is transported towards the die.

The position of the reaction zone in the extruder is dependent on temperature, throughout and the rotation speed of the screws. These parameters also determine the starting point of the reaction, especially the temperature has a large influence. The influence of the other parameters on the position of the reaction zone are marginal. Under normal operation the reaction starts in the partially filled zone.

The fully filled zone or the pump zone is an important feature in the working of the twin screw

[†]Author to whom correspondence should be addressed.

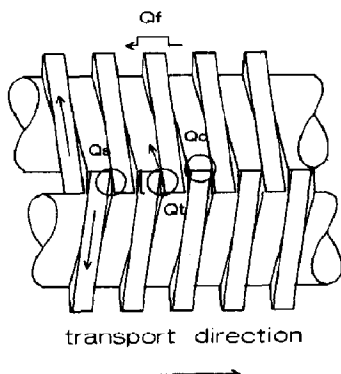


Fig. 1. The leakage gaps in a twin screw extruder.

extruder. It strongly influences the flow profile and therefore the residence time in the extruder. In this zone, near the die, the volumetric displacement of the screws is usually greater than the output volume rate. The difference corresponds to a backwards leakage flow in the extruder through the leakage gaps. The volumetric displacement rate or theoretical throughput equals the number of C-shaped chambers transported per unit time multiplied by the chamber volume:

$$Q_{th} = 2mNV \quad (1)$$

in which N is the screw speed (1/s), m the number of thread starts per screw and V the volume of a C-shaped chamber.

The real volumetric throughput is given by

$$Q = Q_{th} - Q_l \quad (2)$$

where Q_l is the sum of all leakage flows over a cross-section of the extruder. The leakage flow is driven by inter-chamber pressure differences and conveying by the moving surfaces:

$$Q_l = A'N + B' \frac{\Delta P}{\eta} \quad (3)$$

where A' and B' are geometrical constants which can be calculated (Ganzeveld and Janssen, 1990), N the screw speed, ΔP the pressure difference between two consecutive chambers and η the viscosity of the mixture.

In the partially filled length of the extruder no axial pressure gradient exists. However, over the fully filled length the pressure rises to that at the die entry. In a uniform screw system with an iso-viscous Newtonian fluid this pressure development along the screw would be linear. For a fluid with a changing viscosity, like reactive systems, the pressure development is not linear anymore but curved.

The leakage flows can affect strongly the flow profile and therefore the mixing and residence time distribution of material in each individual chamber (Speur *et al.*, 1987). Both play an important role in the reaction process.

THE BASIC MODEL

The numerical modelling of the counter-rotating twin screw extruder is based on a model that approximates the C-shaped chambers as continuous stirred tank reactors (CSTRs) on a conveyor band. The chambers interact with each other through the leakage gaps, both in the partially filled zone and in the fully filled zone. As no axial pressure gradient exists in the partially filled zone, these interactions consist only of the rotational speed dependent part of the leakage flow equations [eq. (3)]. In the fully filled zone, the pressure driven leakage flow also has to be taken into account.

In the model, each chamber is assumed to be perfectly mixed. Although, under certain circumstances, this assumption is an oversimplification, its validity is confirmed by residence time distribution measurements (Janssen *et al.*, 1979). Only if short-cut flows between the leakage gaps occur does the assumption of perfect mixing lead to erroneous results. However, under normal operating conditions the assumption describes the process in the extruder fairly well.

In Fig. 2, the model is schematically represented for single thread screws. The model is based upon the overall balances for enthalpy, mass and concentration that can be derived for each individual chamber moving through the extruder.

The mass balance over the j th chamber equals

$$\begin{aligned} \frac{dM_j}{dt} = \frac{d(\rho_j \varepsilon V_j)}{dt} = \{Q_{t,i} \rho_{j+1} + 2Q_{f,i} \rho_{j+2} + 2m(Q_{t,i} \\ + Q_{s,i}) \rho_{j+2m}\} - \{Q_{t,o} + 2Q_{f,o} \\ + 2m(Q_{c,o} + Q_{s,o})\} \rho_j \end{aligned} \quad (4)$$

in which V_j is the volume of the j th chamber, ε the filling degree of the chamber and ρ_j the density of the material in the j th chamber. Q_t , Q_f , Q_c and Q_s are the leakage flows, where i and o denote inflow or outflow. In the balance the variation of density during the polymerization reaction can be incorporated. However, in the model, this variation will be neglected because the density as a function of concentration is not known. Nevertheless, this relation should be investigated in future as the volume change due to the reaction may be as large as 15%. Assuming a constant density, eq. (4) results in

$$\begin{aligned} \frac{d(\varepsilon V_j)}{dt} = \{Q_{t,i} + 2Q_{f,i} + 2mQ_{c,i} + 2mQ_{s,i}\} \\ - \{Q_{t,o} + 2Q_{f,o} + 2m(Q_{c,o} + Q_{s,o})\}. \end{aligned} \quad (5)$$

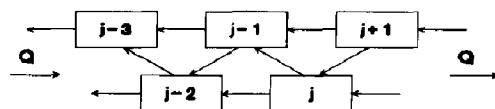


Fig. 2. The reaction model for single thread screws.

Except at the transition between the partially filled and fully filled zone, no accumulation of material will occur in the chamber, for screw sections with a constant chamber volume. The ingoing flow should therefore be equal to the outgoing flow. The achievement of this steady state may be problematic as the pumping action of the twin screw extruder is poor for liquids with a low viscosity. However, during the experiments no serious problems were encountered.

The second relevant balance for the model is the monomer concentration balance which equals

$$V_j \varepsilon \frac{dc_j}{dt} = -\varepsilon V_j R + \{Q_{t,i} c_{j+1} + 2(Q_{f,i} c_{j+2}) + 2m(Q_{t,i} + Q_{s,i}) c_{j+2m}\} - \{Q_{t,o} + 2Q_{f,o} + 2m(Q_{t,o} + Q_{s,o})\} c_j \quad (6)$$

where R is the reaction rate and c_j the concentration of monomer in the j th chamber.

The energy balance is coupled to the monomer concentration balance by the reaction term, as this depends on the monomer concentration and the temperature. The energy balance equals

$$V_j \varepsilon \rho c_p \frac{dT_j}{dt} = -\varepsilon V_j R \Delta H_r + \rho c_p [\{Q_{t,i} T_{j+1} + 2(Q_{f,i} T_{j+2}) + 2m(Q_{t,i} + Q_{s,i}) T_{j+2m}\} - \{Q_{t,o} + 2Q_{f,o} + 2m(Q_{t,o} + Q_{s,o})\} T_j] + hA(T_w - T_j) \quad (7)$$

where c_p is the specific heat, ΔH_r the reaction enthalpy, T_j the temperature in the chamber observed, h the heat transfer coefficient, A the heat exchanging surface of the chamber and T_w the temperature of the wall at the position of the chamber.

The model is based on the changes in a single chamber moving through the extruder. Therefore, the coordinate system is attached to the moving chamber and not to the extruder.

The relation between the time and the position of the chamber in the extruder is determined by the displacement velocity of the chamber through the extruder. This velocity (v_c) equals the product of the rotational speed of the screws (N) and the pitch of the screw at the position of the chamber [$S(x)$]:

$$v_c = NS(x). \quad (8)$$

The position of the chamber in the extruder equals

$$x(t) = N \int_0^t S(x) dt. \quad (9)$$

For a screw with a constant pitch, this results in

$$x(t) = NSt. \quad (10)$$

Additionally, equations for the fully filled length, the heat transfer and the kinetics are necessary to complete the description of the model. The fully filled length is determined by the die pressure, the viscosity profile of the reactive material and the leakage flows.

The die pressure is an input parameter of the model. The viscosity profile can be calculated by a viscosity model. The heat transfer coefficient can be calculated from different theories, of which the coefficient derived by Speur (1988) gives the most accurate results (see the heat transfer description). The reaction kinetics used here describe a first-order bulk polymerization with a superposition of the gel effect (as will be explained later).

Solving the total set of equations numerically for a chosen bulk polymerization leads to profiles for the conversion, molecular weight, temperature and pressure, from which the progress of the reaction in the extruder can be studied.

One extra complication occurs, when validating the model with experimental results, if the reaction is not completed at the end of the extruder. The reactive mixture will also react in the die. For large dies in particular, this may have a notable effect on the final product. Because of the complex geometry of a good extruder die and the shear and elongational effects, it is very complicated to model the reaction process in the die. Nevertheless, to form an impression of the ongoing reaction, the die is approximated as a simple tube with a certain volume in which the material is transported as plug flow. The residence time in the model die equals the residence time in the experimental die.

THE RHEOLOGICAL MODEL

Understanding the rheological properties of polymer-monomer solutions is essential for modelling bulk polymerizations. In reactive extrusion, the hydrodynamic behaviour of the extruder is strongly influenced by the rheological properties. Therefore, to be able to model the extruder as a reactor and to calculate the fully filled length, the viscosity profile of the reactive mixture has to be known.

Stuber (1986) developed an empirical model which accurately describes this viscosity behaviour of the radical bulk polymerization over the whole concentration range. The model is based on known empirical behaviour of polymer solutions. The basis of the model is

$$\eta_0(c, \bar{M}_w, T) = F\xi$$

in which

$$F = K[1 + a_1(c\bar{M}_w)^{0.5} + a_2(c\bar{M}_w)]^{3.4} \quad (11)$$

and

$$\xi = \exp \left[(b_0 + b_1 c + b_2 c^2) \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) + b_3 c^3 \right]$$

where c is the polymer concentration in weight percent, \bar{M}_w the weight average molecular weight of the polymer in thousands, K , a_1 , a_2 , b_0 , b_1 , b_2 and b_3 are constants and T and T_{ref} are temperatures in K . The parameter T_{ref} adjusts the concentration dependence of the viscosity model at low concentrations. As

T_{ref} decreases, the concentration dependence for low concentrations decreases.

The equation was used to predict accurately the solution viscosity data for the polymerization of methylmethacrylate (MMA). By adjusting the constants, the viscosity model can also be used for other polymerization reactions.

In our case, the bulk polymerization reaction investigated in the extruder is the polymerization of butylmethacrylate (BMA). For this reaction, no useful rheological data exist which could be applied to the model in order to adjust the constants. However, the behaviour of the BMA/PBMA solution can be expected to be very similar to the MMA/PMMA solution, due to the similarity in their molecular structure (Lachinov *et al.*, 1978; Pezzin, 1966). Therefore, the viscosity model for MMA/PMMA should predict the rheological behaviour of the BMA/PBMA solution fairly accurately.

Only the absolute viscosities of the BMA/PBMA mixture have to be adjusted due to the larger mobility of the molecules which decreases the viscosity and decreases the concentration dependence at low concentration of the polymer. This is done by adjustment of the reference temperature in the model presented by Stuber from 465.15 to 400.15 K. The remainder of the values used for the rheological model of the BMA/PBMA mixture are equal to the values used by Stuber for the MMA/PMMA solution. Model results were compared with the little data available (Yemelyanov *et al.*, 1982) and appeared to agree reasonably well. The values of the constants for the BMA/PBMA solution are given in Table 1.

The rheological model obtained is used to predict the viscosity profile in the extruder under different reaction circumstances and to determine the fully filled length of the extruder.

The model does not take the influence of shear rate on the viscosity into account. For the reaction used the dependence of the viscosity of the polymer-monomer mixture on shear is already small. Although the changes of viscosity in the leakage gaps due to non-Newtonian effects can influence the pressure built up, and therewith the fully filled length, the viscosity

changes associated with the progress of the reaction and changing temperature are far more superior.

THE HEAT TRANSFER MODEL

During the bulk polymerization reactions in the extruder, a large amount of heat is released. Heat transfer is therefore an important process parameter. Several heat transfer models exist based on the penetration theory, almost all in the area of single screw extruders (Jepson, 1953; Mohr *et al.*, 1957; Janeschitz-Kriegl and Schijf, 1969; Janssen *et al.*, 1975).

Speur (1988) derived an empirical model for the heat transfer coefficient in a counter-rotating twin screw extruder which was used in the modelling. The heat transfer coefficient was determined from the energy balance for a single C-shaped chamber interacting with its neighbours:

This heat transfer coefficient is dependent upon the rotational speed and the relative throughput of the extruder (α_r):

$$h = 410 \left(\frac{N}{0.174} \right)^{1.65 - 2.36\alpha_r} \quad (12)$$

It is particularly significant that for all experiments the value of this heat transfer coefficient exceeds the value of the heat transfer coefficient as calculated by penetration theory. This may be attributed to an additional convective effect associated with the flow pattern in the chamber. Also the heat transfer through the flights of the screw, which is neglected in the penetration theory, may have a positive effect on the total heat transfer.

THE KINETIC MODEL

Bulk polymerizations of acrylates are free radical addition polymerizations. With this type of reaction, polymer chains are formed in a relatively short time and subsequently excluded from further participation in the reaction process. The chain formation can be divided into three steps:

- initiation or chain start
- propagation or chain growth
- termination or chain stop.

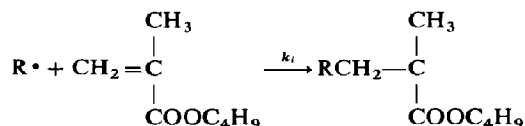
With these types of reactions, the velocity of the termination step varies during the polymerization, leading to the occurrence of the so-called Trommsdorff or gel effect which causes an abrupt increase of the propagation velocity.

The progress of the BMA polymerization looks as follows:

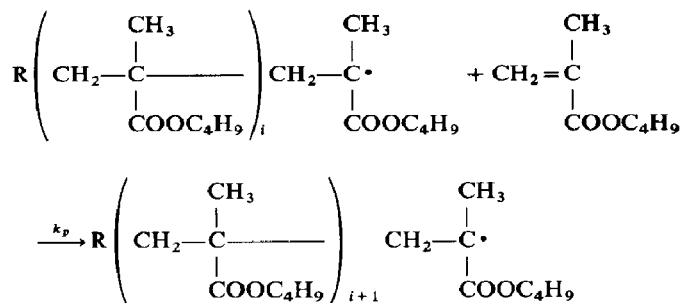
Table 1. Values of constants used in the rheological model

K	0.00216	b_0	600
a_1	0.125	b_1	80
a_2	3.75×10^{-11}	b_2	1
T_{ref}	400.15	b_3	1.2×10^{-5}

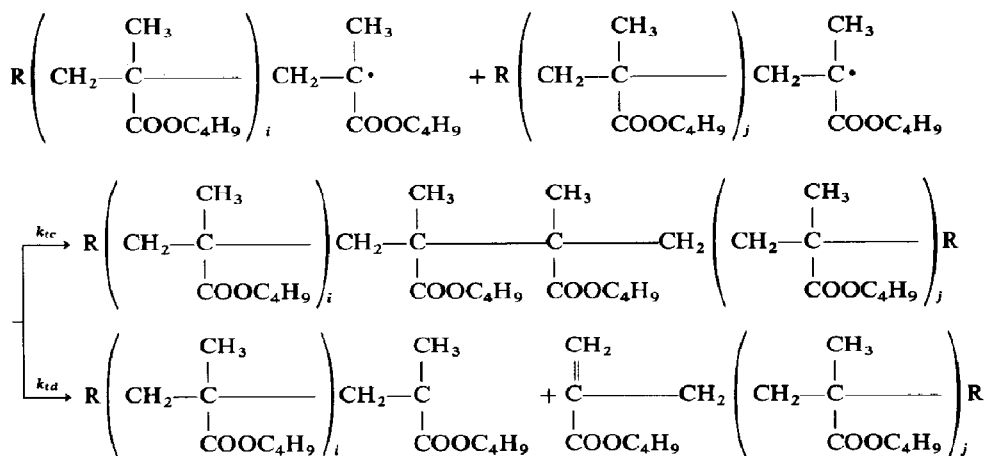
initiation:



propagation:



termination:



in which k_i , k_p , k_{tc} and k_{td} are, respectively, the reaction constants for the initiation reaction, the propagation reaction, the termination by combination and the termination by disproportionation.

Due to the appearance of the aforementioned gel effect at a certain instance during the reaction, the reaction progresses in two stages:

- The first stage, the beginning of the reaction, can be described by the conventional kinetics also used for diluted polymer systems. In this stage, the polymerization of butylmethacrylate is a first-order reaction in the monomer concentration.
- The second stage in the reaction progress is reached when the conversion has increased to a certain point. The reaction mixture has become more and more viscous, leading to a limitation in the mobility of the polymer chains.

The termination reactions are now controlled by diffusion limitation, resulting in a reduced termination reaction constant k_t (Trommsdorff *et al.*, 1947; Cardenas and O'Driscoll, 1976). Due to the reduced k_t , the amount of polymer radicals increases, resulting in an abrupt increase of the propagation velocity, called the gel effect or Trommsdorff-effect. The appearance of the gel effect leads to a higher conversion and

a drastic increase of the average molecular weight of the polymer formed. No simple equations for the reaction velocity at this stage of the polymerization exist. However, the second stage does play an important role in the reactive extrusion process.

To be able to simulate the bulk polymerizations, Marten and Hamielec (1979) have proposed a semi-empirical model which includes the gel effect. The model is based on the free-volume theory for which two problems have to be solved:

- (1) Determination of the conversion at which significant chain entanglements first occur.
- (2) Development of a relationship which gives the decrease in the termination rate constant as a function of temperature and polymer weight and concentration.

The solution of the problems leads to the following relation for the termination constant k_t :

$$\frac{k_t}{k_{t_0}} = \left(\frac{\bar{M}_{wcr1}}{\bar{M}_w} \right)^a \exp \left[-A \left(\frac{1}{V_F} - \frac{1}{V_{Fcr1}} \right) \right] \quad (13)$$

where k_{t_0} is the initial termination rate constant, \bar{M}_{wcr1} is the critical weight average molecular weight at the conversion where the gel effect starts, \bar{M}_w is the weight average molecular weight, a is a constant

which value depends on the stage of the polymerization, A is a constant, V_F is the free volume and V_{Fcr1} is the critical free volume at the onset of the gel effect.

The free volume can be calculated from

$$V_F = [0.025 + \alpha_p(T - T_{gp})] \frac{V_p}{V_T} + (0.025 + \alpha_m(T - T_{gm}) \frac{V_m}{V_T} \quad (14)$$

where the indices p and m denote polymer and monomer and $\alpha = \alpha_l - \alpha_g$, α_l is the expansion coefficient for the liquid state, α_g the expansion coefficient for the glassy state, T_g the glass transition temperature, V the volume and V_T is the total volume.

The critical free volume is determined by

$$K_3 = \bar{M}_{wcr1}^m \exp(A/V_{Fcr1}). \quad (15)$$

K_3 is a constant which is dependent upon temperature and determined empirically, m is arbitrarily set equal to 0.5 and A is a constant.

The combination of the equations leads, for a bulk polymerization above the glass transition temperature, to a general rate expression:

$$\frac{dx}{dt} = k_p \left(\frac{f_{kd}}{k_{io}} \right)^{0.5} \frac{(1-x)}{(1-\varepsilon x)} [I]_0^{0.5} \exp(-k_d t/2) \times \left(\frac{\bar{M}_w}{\bar{M}_{wcr1}} \right)^a \exp \left(\frac{A}{2} \left(\frac{1}{V_F} - \frac{1}{V_{Fcr1}} \right) \right) \quad (16)$$

where k_d is the reaction constant for the decomposition of the initiator, f the efficiency factor of the initiator, k_{io} is the initial termination constant, x the degree of conversion, ε the volume contraction factor $(d_p - d_m)/d_p$, d_p is the density of the polymer, d_m is the density of the monomer, $[I]_0$ is the initial initiator concentration and t is the time.

For the first stage of the polymerization, the constants a and A have to be zero as no gel effect is present. However, as the termination reaction becomes diffusion limited and the gel effect starts to occur, values for a and A have to be determined. Both values are estimated using a fit to some of the experimental data.

Finally, the development of the molecular weight as a function of the conversion has to be known. Marten and Hamielec state this relation to be

$$\text{cum } \bar{M}_w = \frac{2M_0}{x} \int_0^x \frac{dx}{\tau} \quad (17)$$

where M_0 is the molecular weight of the monomer and τ the reciprocal instantaneous number average degree of polymerization.

By solving eqs (16) and (17) simultaneously, the conversion-time history can be obtained. However, due to the already complicated reaction situation in the extruder, the simultaneous solving of these balances is not practicable. Also, the agreement between the experimentally measured \bar{M}_w and the \bar{M}_w calculated by the Marten and Hamielec model is rather

poor. Therefore, a new expression for the relation between the instantaneous weight average molecular weight and the conversion [eq. (17)] has to be found.

This expression can be found by looking at the outcomes of the experiments of the polymerization of MMA and BMA. It shows that in the gel effect area the relation between the molecular weight and the conversion can almost be assumed to be a straight line (Ganzveld, 1992; Marten and Hamielec, 1979). This is, of course, an oversimplification of the relation but very useful for the modelling of the extruder as will be established later. Based on this experimental data, eq. (17) is now assumed to be equal to

$$\bar{M}_w = 781 \cdot \text{conversion} - 6500 \quad (18)$$

where the conversion is in weight percentage.

With eqs (16) and (18), the reaction kinetics can now be solved for reactive extrusion. The constants and parameters used in these equations are a combination of the data used by Marten and Hamielec for MMA polymerization and data available on the BMA polymerization and components. The first are used as a substitute for lacking BMA data. As MMA and BMA are similar in chemical structure, this substitution should still result in reliable reaction data. Therefore, the constants A , K_3 , V_{Fcr1} and T_{gm} are data of Marten and Hamielec. T_{gp} , α_m , α_p , \bar{M}_{wcr1} and ε are literature data on BMA and PBMA (Brandrup and Immergut, 1989; Pezzin, 1966). The constant a is adjusted on the basis of our own experimental data on the polymerization of BMA in the extruder. The constants used are presented in Table 2.

COMPARISON BETWEEN THE SINGLE-COMPONENT REACTION MODEL AND THE EXPERIMENTS

By comparing the model with experimental results and analysis of the validity of the assumptions and omissions in the numerical program can be performed. It also gives an insight into the consequences of simplifications which are present in a numerical model.

Experimental set-up

A mixture of *n*-butylmethacrylate (inhibited), with a combination of a fast initiator and a slow initiator was fed to the extruder, at room temperature. The fast initiator assumes a start of the reaction at relatively low temperatures and therefore decreases the maximum temperature in the extruder, whereas the slow initiator is still active towards the end of the process, when temperatures are high. The mixture and the

Table 2. Values of constants used for the kinetic model of BMA

A	1.11	α_m	1×10^{-3}
a	0.01	α_p	5×10^{-4}
K_3	2.7×10^5	\bar{M}_{wcr1}	30,000
T_{gm}	167 K	V_{Fcr1}	0.151
T_{gp}	293 K	ε	0.154

extruder were both flushed with nitrogen to prevent an extra inhibition of the reaction.

The mixture was extruded in a 40 mm Rollepaal counter-rotating twin screw extruder ($L/D = 15$). The extruder has five heating zones with which a temperature profile over the extruder can be established. The basic settings of the extruder are

concentration slow initiator	1.2%
concentration fast initiator	0.5%
screw speed	0.63 1/s
die pressure	0 Pa
throughput	26.2 g/min
inlet temperature	20°C
wall temperatures	20, 120, 130, 130, 120°C
die temperature	110°C.

The different parameters were varied one at a time while the other parameters remained those of the basic setting. The pressure profile over the extruder was measured with three pressure transducers. The output of the extruder ranged from 1.2 to 2.9 kg/h. The samples collected for the different reaction circumstances were directly frozen in liquid nitrogen to stop the reaction immediately. The samples were analyzed for conversion and number and weight average molecular weight. The conversion of the polymerization reaction was determined gravimetrically. The molecular weight of the samples is determined by gel permeation chromatography.

The comparison

A direct comparison between the experiments and the simulations showed a good agreement for almost all parameters (Figs 3–8). In most circumstances, both the experimentally determined conversions and the molecular weights agree reasonably well with the calculated results. The minor deviations may be attributed to the use of simplifications in the rheological and kinetic model.

However, a large disagreement is visible when the results of the simulation of the progress of the reaction at increasing screw speed with no fully filled length

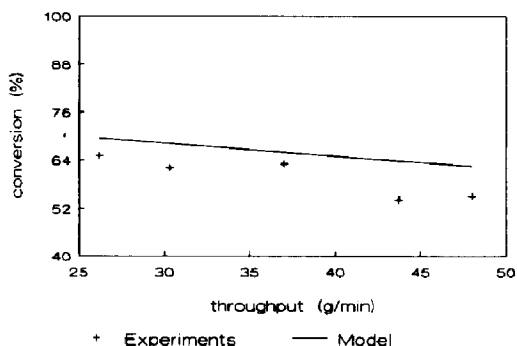


Fig. 3. A comparison between the experimentally and numerically obtained conversions for an increasing throughput ($N = 0.63$ 1/s and $P_{die} = 0$ bar).

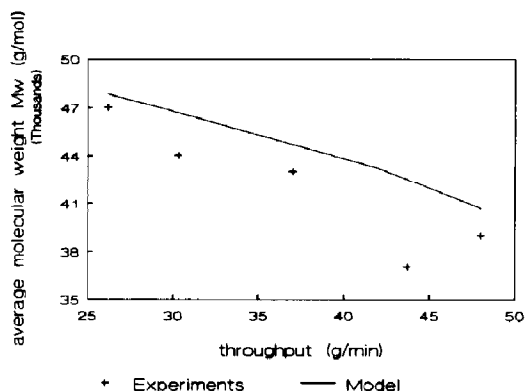


Fig. 4. The comparison of the molecular weights obtained for an increasing throughput ($N = 0.63$ 1/s and $P_{die} = 0$ bar).

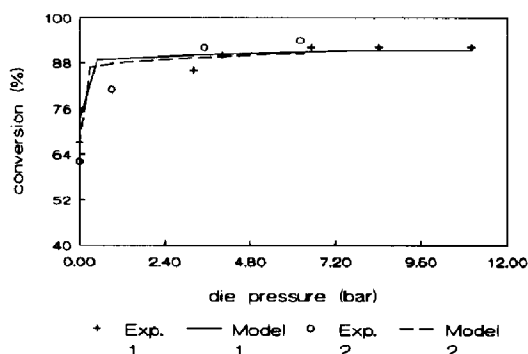


Fig. 5. The conversion as a function of the die pressure for the experimental and numerical data ($N = 0.63$ 1/s). Situation 1: $Q = 20.3$ g/min, situation 2: $Q = 31.0$ g/min.

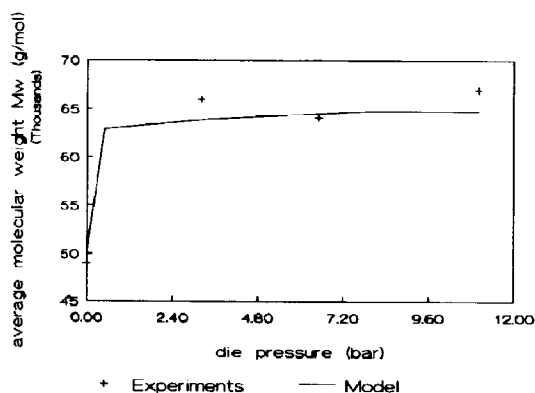


Fig. 6. The molecular weight as a function of the die pressure for model and experiments ($Q = 20.3$ g/min, $N = 0.63$ 1/s).

present are compared with the experiments (Fig. 9). Where the experiments show an independence of the rotation rate of the screws, the model shows a decrease. Also, the calculated conversions at low rotation rates are much higher than observed during the

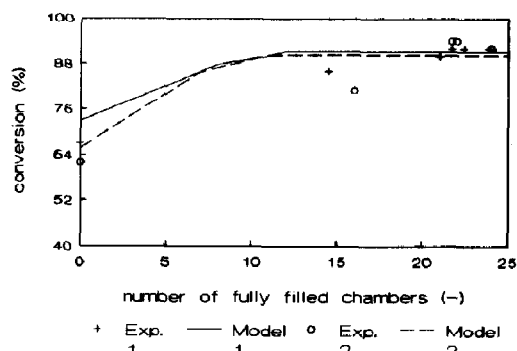


Fig. 7. A comparison between the predicted and modelled influence of the fully filled length on the conversion of the reaction ($N = 0.63$ l/s) situation 1: $Q = 20.3$ and 2: $Q = 31.0$ g/min.

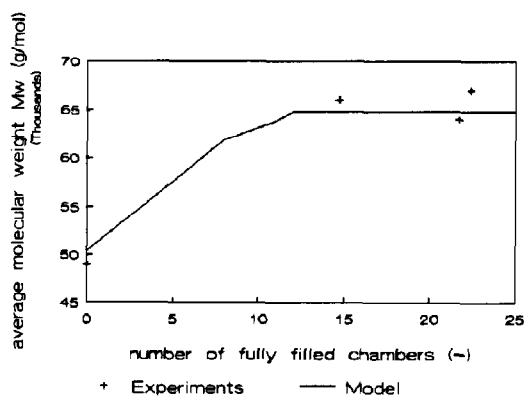


Fig. 8. A comparison between the predicted and modelled influence of the fully filled length on the molecular weight of the reaction ($Q = 20.3$ g/min and $N = 0.63$ l/s).

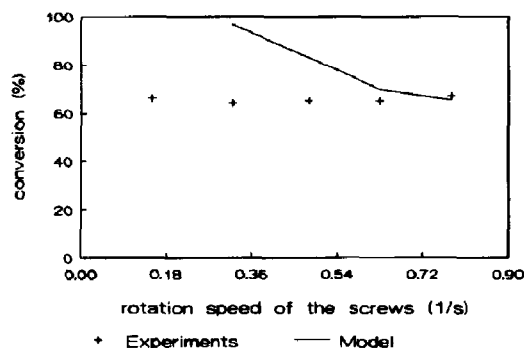


Fig. 9. The influence of the rotation rate of the screws on the conversion; a comparison between the model and the experiments ($Q = 26.2$ g/min and $P_{die} = 0$ bar).

experiments. This is probably due to a lower material temperature caused by the formation of a polymer barrier at the barrel wall at low rotation rates of the screws. It results in a lower overall reaction constant,

leading to the lower conversions observed. However, this explanation is not experimentally verified.

Nevertheless, if a fully filled length is present or the rotational speed is high, as both is the case in industrial processes, the result of the model agree well with the experiments (Fig. 9).

MODEL PREDICTIONS

Next to a direct comparison of the model results and the experimental data obtained, the model can also be used to predict the progress of the reaction in the extruder. To investigate the influence of extruder and reaction parameters on the reaction process, several situations are simulated.

One of the limitations for the use of an extruder as a reactor is the reaction enthalpy. Therefore, it is interesting to study the effect of a significant rise in the heat of reaction on the temperature profile in the extruder. For both simulations it is assumed that the reaction kinetics are equal to the kinetics of BMA. The extruder settings are:

- rotational speed: 0.50 l/s
- throughput: 0.60 g/s
- wall and die temperatures: 120, 130, 130, 120, 110°C
- die pressure: 0 bar.

Figure 10(a) and (b) show the progress of the reaction

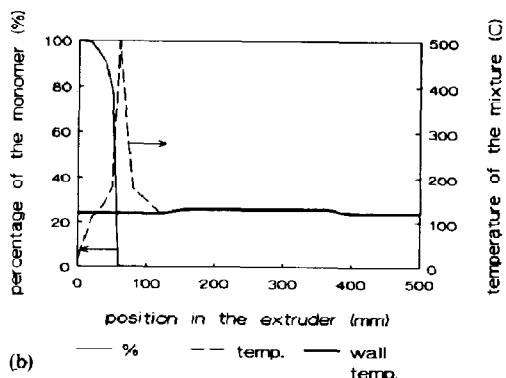
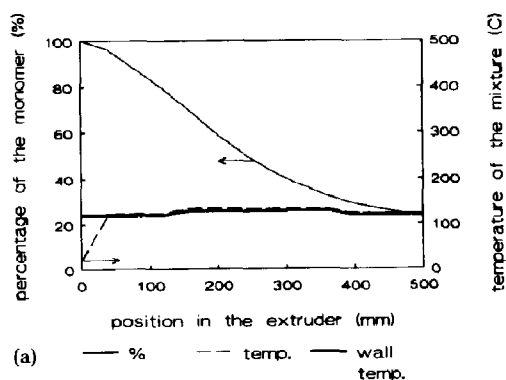


Fig. 10. The influence of the reaction enthalpy on the reaction progress ($Q = 37.6$ g/min, $N = 0.50$ l/s and $P_{die} = 0$ bar): (a) $\Delta H_r = 56.5$ kJ/mol, (b) $\Delta H_r = 180$ kJ/mol.

in the extruder for two different reaction enthalpies. It is apparent that the reaction enthalpy not only has an influence on the maximum temperature reached in the extruder but that the conversion is also clearly affected. At a reaction enthalpy of 56.5 kJ/mol (BMA), the temperature hardly deviates from the wall temperature and the maximal conversion is only 80%. A reaction enthalpy of 180 kJ/mol, on the other hand, causes a drastic increase in the maximum temperature of the material in the extruder, whereas a 100% conversion is already reached after 1/6 of the length of the extruder. The sharp increase in the mixture temperature was not present in simulations with a reaction enthalpy below 160 kJ/mol. Only moderate temperature increases of 30°C are reached for these situations, which are often acceptable for production processes. Nevertheless, reactions with a reaction enthalpy in the order of 150 kJ/mol, and with reaction kinetics similar to the butylmethacrylate polymerization, should be processed with caution in the type and size of the extruder used for the simulation. This conclusion is, of course, valid within the limitations of the simulation program.

Another parameter which can cause a too high material temperature in the reactor are the wall and die temperatures. An increase of the wall temperature in the first part of the extruder causes the reaction front to move towards the feed end as the reaction components reach the reaction temperature earlier. This results in a longer reaction time in the extruder and therefore a higher conversion of the reaction and a possible higher temperature of the product. A decrease of the wall temperature in this part causes the opposite effect, namely, the shift of the reaction front towards the die leading to shorter effective residence times, lower conversions and lower material temperatures. Two wall temperature profiles are simulated, the results of which are presented in Fig. 11.

From the simulations it can be concluded that the conversion is significantly influenced by a change in the temperature profile. However, the maximum tem-

perature the mixture reaches in the extruder is hardly affected by a change in the wall temperature, unlike the effect of a change in the reaction enthalpy.

The moving of the reaction front can also be caused by the rotational speed. The rotational speed influences the position of the reaction zone in the extruder. A high rotational speed causes the reaction front to move towards the die. This indicates that if the screw speed is too high the situation could occur in which the reaction does not take place in the extruder at all. However, a higher rotational speed results in a larger theoretical throughput thereby also permitting a higher throughput. As the movement of the reaction front now limits the rotational speed which can be used, the throughput for the process also becomes limited, thus restricting the working area.

The boundaries of the restricted working area are very important, especially for industry. However, simulations show that if a fully filled length is present in the extruder, the effect of the rotational speed on the reaction process is marginal.

Only if the die pressure is zero, a non-desirable situation in most processes, does the rotational speed have a considerable influence on the reaction progress (Fig. 12).

The die pressure has a major influence on the reaction process. The residence time is largely dependent on the fully filled length and, consequently, on the die pressure. Therefore, the conversion of the reaction is, to a large degree, determined by the die pressure. This is visualized in Fig. 13.

A complete simulation for a single experiment is shown in Fig. 14(a)–(c). The extruder settings are:

- rotational speed: 0.631/s
- throughput: 0.34 g/s
- wall and die temperatures: 120, 130, 130, 120, 110°C
- die pressure: 11 bar.

The influence of the gel effect on the reaction progress, specifically on the molecular weight of the poly-

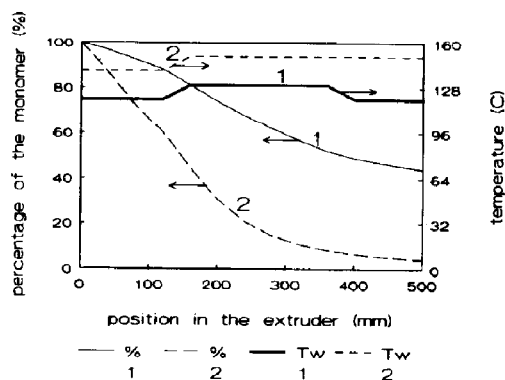


Fig. 11. The effect of the temperature profile on the reaction, ($Q = 20.3$ g/min and $P_{die} = 0$ bar). Situation 1: temperature profile 120, 130, 130 and 120°C; situation 2: temperature profile 140, 150, 150 and 150°C.

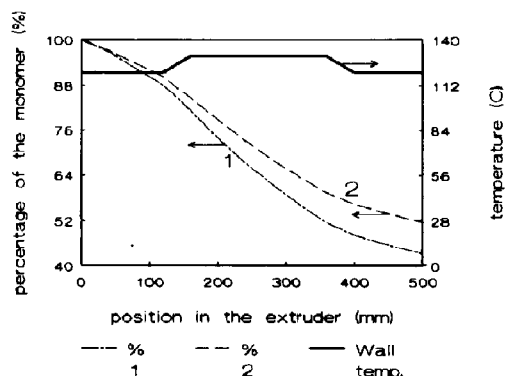


Fig. 12. The dependence of the reaction progress on the rotation rate ($Q = 26.3$ g/min and $P_{die} = 0$). Situation 1: $N = 0.631$ s; situation 2: $N = 0.781$ s.

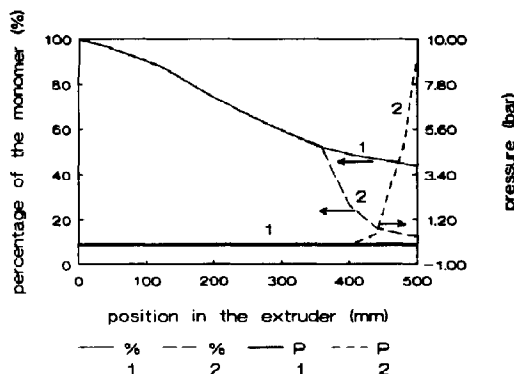


Fig. 13. The influence of the die pressure on the reaction progress ($\dot{Q} = 20.3$ g/min and $N = 0.63$ l/s). Situation 1: $P_{\text{die}} = 0$ bar; situation 2: $P_{\text{die}} = 11$ bar.

mer formed at each position, is very clearly illustrated in Fig. 14(c). During the first stage of the polymerization \bar{X}_n , the instantaneous formed number average degree of polymerization, decreases with reaction time. This implies a decrease in the molecular weight of the polymer formed as it moves through the extruder. However, as the polymerization reaches the gel stage the molecular weight of the polymer formed increases drastically due to the decrease of the termination rate.

This also results in a large increase of the viscosity as a result of the relation between viscosity and molecular weight, visualized in Fig. 14(b).

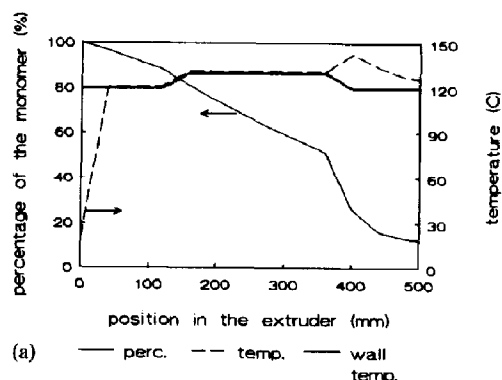
CONCLUSIONS

Computer models are very useful tools in understanding the behaviour of the extruder as a polymerization reactor. The influences of several reaction and extruder parameters can be analyzed theoretically, thereby avoiding the costs incurred by expensive experiments. The computer model can also be used to determine the limitations of the use of the extruder as a reactor and to study the effects scale-up would have on the process. The validity of these analyses are, of course, directly related to the exactness of the model. Therefore, the assumptions and approximations used in the modelling should be verified for each situation.

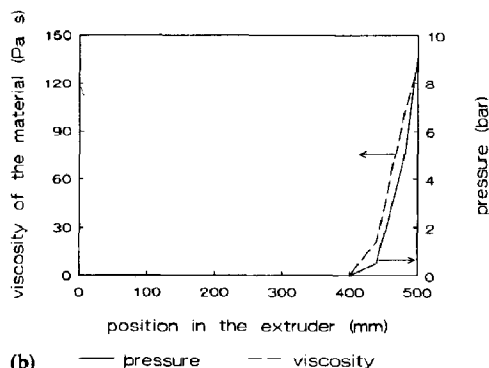
The conclusions which can be drawn from the numerical modelling of a single-component reaction (the polymerization of *n*-butylmethacrylate) in a twin screw extruder are:

— A comparison between the experimental and numerical data shows a good agreement for almost all parameters. The model describes the reactive extrusion process reasonably well. However, for low rotation rates, disagreements may occur between the experimental and the predicted data.

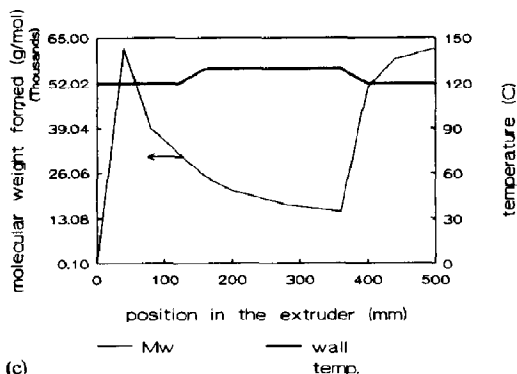
— For a precise modelling of the extruder, extended investigations into the kinetics of polymerization reactions in bulk, the rheology of reactive mixtures and the heat transfer mechanism have to be carried out.



(a) — perc. — temp. — wall temp.



(b) — pressure — viscosity



(c) — Mw — wall temp.

Fig. 14(a). The concentration and temperature profile for the given experiment. (b) The viscosity and pressure profile for the given experiment. (c) The molecular weight of the polymer formed during the reaction progress in the extruder.

— Also, the volume of the die has a noticeable effect on the end product. Judicious combination of extruder parameters and die properties may lead to processes less sensitive to disturbances.

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NOTATION

a	the thermal diffusivity, m^2/s
A	the heat exchanging surface, m^2
A'	a geometrical constant m^3

B'	a geometrical constant, m^3
c	the polymer weight percentage, dimensionless
c_p	the specific heat, J/kg K
C	concentration, mol/m^3
C_j	the concentration in the j th chamber, mol/m^3
C_i	the concentration in chamber i , mol/m^3
d_p	the density of the polymer, kg/m^3
d_m	the density of the monomer, kg/m^3
f	efficiency factor of the initiator, dimensionless
F	the structure factor, Pa s
h	the heat transfer coefficient, $J/m^2 s K$
ΔH_r	the reaction enthalpy, J/mol
$[I]$	the initiator concentration, mol/m^3
$[I]_0$	the initial initiator concentration, mol/m^3
k_d	the decomposition constant, 1/s
k_i	the initiation constant, $m^3/mol s$
k_p	the propagation constant, $m^3/mol s$
k_{tc}	the termination by combination constant, $m^3/mol s$
k_{td}	the termination by disproportionation constant, $m^3/mol s$
K	a constant, Pa s
m	the number of thread starts per screw, dimensionless
M	the monomer, dimensionless
M_0	the molecular weight of the monomer, g/mol
\bar{M}_w	the weight average molecular weight, g/mol
\bar{M}_{wcr1}	the weight average molecular weight at onset gel effect, g/mol
N	the rotation rate of the screws, 1/s
P_{die}	the die pressure, Pa
ΔP	the pressure difference between two consecutive chambers, Pa
Q	the throughput, m^3/s
Q_c	the leakage flow through the calender gap, m^3/s
Q_f	the leakage flow through the flight gap, m^3/s
Q_i	the flow from position i , m^3/s
Q_t	the total leakage flow, m^3/s
Q_s	the leakage flow through the side gap, m^3/s
Q_t	the leakage flow through the tetrahedron gap, m^3/s
Q_{th}	the theoretical throughput, m^3/s
R	the reaction velocity, $mol/m^3 s$
S	the pitch of the screw, m
t	time, s
T	the temperature, K
T_j	the temperature in chamber j , K
T_i	the temperature in chamber i , K
T_g	the glass transition temperature, K
T_p	the temperature of the polymer, K
T_w	the wall temperature, K
V	the volume of the C-shaped chamber, m^3
V_c	the chamber velocity, m/s
V_m	filled volume of a chamber, m^3
V_F	the free volume, m^3
V_{Fcr1}	the free volume at the onset of the gel effect, m^3
x	the degree of conversion, dimensionless

Greek letters

α	the expansion coefficient, m^3/K
α_l	the expansion coefficient for the liquid state, m^3/K
α_g	the expansion coefficient for the glassy state, m^3/K
α_r	the relative throughput, dimensionless
ε	the volume contraction factor, dimensionless
η	the viscosity of the material, Pa s
η_0	the zero shear viscosity, Pa s
ρ	the density, kg/m^3
ρ_i	the density of component i , kg/m^3
ξ	the monomer friction coefficient, dimensionless
%	the percentage of the monomer left, dimensionless

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